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Gregory R. Yandek & Joseph M. Mabry (AFRL/RZSM)

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Air Force Research Laboratory (AFMC)
AFRL/RZSM
9 Antares Road
Edwards AFB CA 93524-7401

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The mechanical properties and environmental durability of engineering thermoplastics are generally dependent on their degree of molecular ordering. Processing conditions affect observed microstructures in this class of materials and costly annealing procedures can be required to generate adequate levels of crystallinity. It is therefore beneficial to not only develop an undestanding of the fundamental physics governing ordering transitions, but to be able to use such knowledge to assert control over crystallization on both morphological and temporal scales.

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CRYSTALLIZATION AUGMENTATION OF ENGINEERING THERMOPLASTICS THROUGH DISPERSION OF SILICON-CONTAINING NANOPARTICLES

Gregory R. Yandek and Joseph M. Mabry

Propulsion Materials Applications Branch
Air Force Research Laboratory
10 E. Saturn Boulevard
Edwards AFB, CA 93524

Introduction

The mechanical properties and environmental durability of engineering thermoplastics are generally dependent on their degree of molecular ordering. Processing conditions affect observed microstructures in this class of materials and costly annealing procedures can be required to generate adequate levels of crystallinity. It is therefore beneficial to not only develop an understanding of the fundamental physics governing ordering transitions, but to be able to use such knowledge to assert control over crystallization on both morphological and temporal scales.

Poly(ether-ether-ketone) (PEEK) enjoys significant industrial utility due to its rapid crystallization rate during cooling. It would be advantageous to utilize other types of engineering thermoplastics in certain applications; however, they are often limited by their ability to crystallize from the molten state. Poly(ether-ketone-ketone) (PEKK) is one such material that suffers from this drawback due to the relative stiffness of its backbone imparted by the additional ketone group.

The influence of the incorporation of silicon-based particles on the crystallization rates of various polymers has been widely demonstrated in the literature.[1-10] Crystallization enhancements have been shown to stem from a reduction in the activation energy involved in the transition as well as from dispersed particles acting as heterogeneous nucleation sites. The extent of benefit has been shown to depend on the level of dispersion of the particles in the polymeric host as a function of the chemical nature of their organic periphery. An optimally tailored nucleating agent for crystallization enhancement should depend on the underlying physics of crystallization of the polymer in question as different species of macromolecules form nuclei homogeneously in a variety of ways.

Despite the significant available body of literature on this subject matter, investigations concerning the augmentation of the crystalline behaviors of engineering thermoplastics are currently few in number. In light of this and in conjunction with an emerging need for advanced yet cost-effective polymeric materials in many applications, a study has been undertaken to determine how the presence of particles, viz. polyhedral oligomeric silsesquioxanes (POSS) and nanosilica, dispersed in PEKK, affect the crystallization kinetics of this particular engineering thermoplastic.

Experimental

Materials. Poly(ether-ketone-ketone) (PEKK) was supplied in powder form from Cytec engineered materials. Phenethyl$_8$T$_8$ (PhEt) was synthesized in our laboratory using an undisclosed procedure. The chemical structures of the repeat unit of PEKK in addition to that of PhEt are depicted in **Figure 1(b&c, respectively)**. Aerosil R150 fumed nanosilica devoid of surface treatment (hydrophilic) and Aerosil R202, treated with polydimethylsiloxane (hydrophobic) were purchased from Degussa with BET surface areas of 150 in^2/g translating into an average particle size of 14 nm.

Instrumentation. Polymer crystallization was monitored using differential scanning calorimetry (DSC) carried out on a TA Instruments Q100 under a nitrogen blanket either isothermally or at scanning rates of 10°C/minute, measuring exothermic signatures indicative of the occurrence of ordering transitions. Rheometry was conducted on an Anton Paar MCR 500 rheometer in parallel plate configuration (gap width = 1.5 mm) at a temperature of 340°C with a strain of 0.5%.

Blend Preparation. Melt processing and blending of PEKK with nanoparticles was conducted on a DSM Micro 15 Compounder with a chamber free volume of 15 cm^3. Powders were pre-mixed in their appropriate ratios and charged to the compounder imposing a residence time of five minutes under an inert nitrogen atmosphere with a flat modular heating

profile of 340°C. Blend extrudates were transferred to a DSM micro-injection molding machine for the fabrication of disks for viscometry, otherwise resultant extrudates were sectioned for DSC analysis.
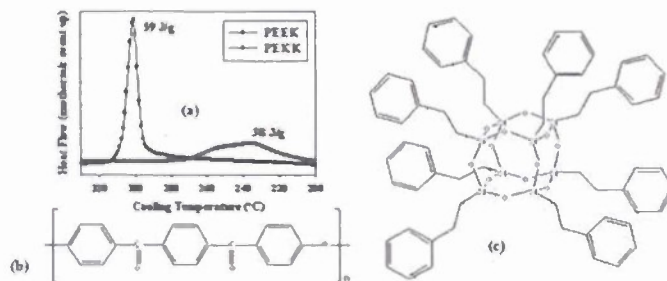

Figure 1. (a) Crystallization exotherms of PEEK and PEKK cooled from the molten state as measured by DSC, (b) chemical structure of the repeat unit of PEKK, and (c) the chemical structure of phenethyl$_8$T$_8$ POSS.

Results and Discussion

Effects of Nanoparticle Dispersion on the Crystallization Kinetics of PEKK. During the crystallization process of polymers, the formation of the precursors (seeds) in homogeneous nucleation can consume a considerable amount of time, especially in the case of a more rigid chemical species, dependant of course on the imposed degree of supercooling. As shown in Figure 1(a), PEKK is far more sluggish in terms of ordering in comparison with PEEK as indicated by the measured exotherms concomitant with the crystallization process. A strategic selection of nucleating agents could circumvent the necessity for PEKK to form the initial long-range structures required to serve as crystallization templates.

Non-isothermal cooling scans of the investigated blends from the molten state indicate that low concentrations of the silicon-containing nanoparticles (1-2%) improve the crystallization kinetics of PEKK as demonstrated in **Figure 2**, where the peak crystallization temperatures shift to higher temperatures during the cooling scans in comparison with the control.
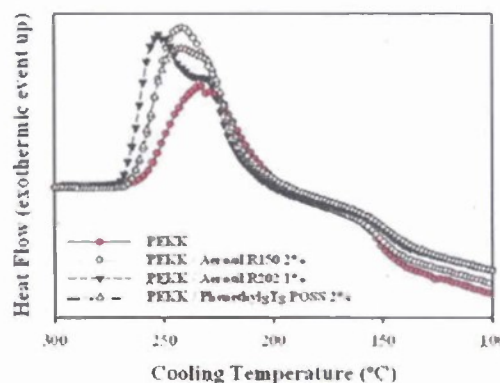

Figure 2. Non-isothermal DSC scans of nano-modified PEKK materials in comparison with the control cooled form the molten state (340°C).

To quantify the benefits resulting from nanoparticle incorporation, isothermal DSC experiments were conducted at the optimal crystallization temperature of the subject grade of PEKK (240°C, determined from experimentation) as well as the lowest temperature that an exothermic signal could be detected (204°) where the crystallization process is severely diffusion-limited. Interestingly, the presence of the nanoparticles has a greater impact on the crystallization kinetics with a reduction in annealing temperature as demonstrated in **Figures 3 and 4**, where relative crystallinity conversions are plotted against heat treatment time as determined by DSC. In both cases, the addition of 1% by weight of Aerosil R202 proves to have the most beneficial impact, improving the crystallization half-time of PEKK by approximately 40% at 240°C and 50% at 204°C. Of particular interest, the

achievement of relatively full crystallinity of the blends occurred in less than 20 percent of the time required for that of the control material.
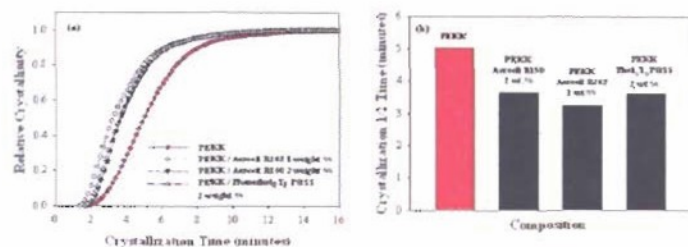

Figure 3. (a) Development of relative crystallinity of the nano-modified blends in comparison with that of the homopolymer, and (b) a comparison of their crystallization half-times. Both sets of data were measured at the optimal crystallization temperature of the subject grade of PEKK (240°C).
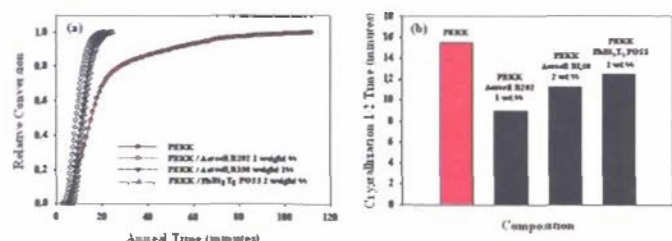

Figure 4. (a) Development of relative crystallinity of the nano-modified blends in comparison with that of the homopolymer, and (b) a comparison of their crystallization half-times. Both sets of data were measured at the lowest-measurable crystallization temperature of the subject grade of PEKK (204°C).

It is also noteworthy to point out that the apparent degrees of achieved crystallinities of the nano-modified materials exceeded those observed for the PEKK homopolymer, especially as the isothermal annealing temperature was lowered, as shown qualitatively in **Figure 5** through an examination of the area corresponding to each melting peak measured by DSC subsequent to heat treatment.
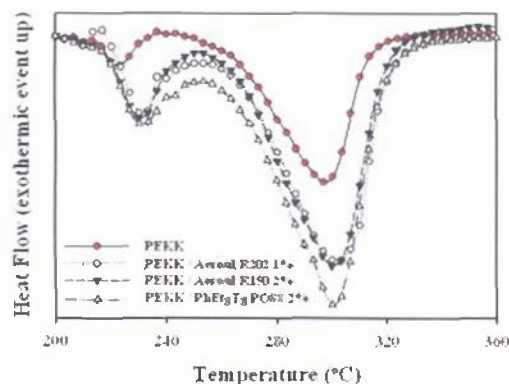
Figure 5. Melting endotherms of homopolymer and nano-modified PEKK as measured by DSC subsequent to annealing at 204°C until cessation of the exothermic signal was measured.

Effects of Nanoparticle Dispersion on the Viscosity of PEKK. The complex viscosities as a function of angular frequency of the homopolymer and nano-modified PEKK materials were measured using a parallel plate rheometer. As illustrated in **Figure 6**, the incorporation of low concentration of silicon-containing nanoparticles reduces the viscosity of the polymer nearly an order of magnitude, presumably through a reduction in inter-chain contacts and overall degree of hydrogen bonding.
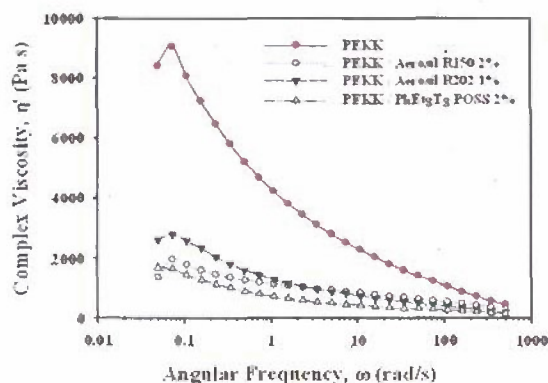
Figure 6. Complex viscosity plotted as a function of angular frequency for PEKK and nano-modified blends.

Conclusions

Low concentrations of silicon-containing nanoscale materials were blended with PEKK to study their effects on polymer crystallization kinetics. Incorporation of nanoparticles into the polymer host material resulted in improved crystallization rates, in some instances as much as doubled. The extent of impact appears to be a function of the degree of supercooling as the nanoparticles demonstrated greater effectiveness at lower temperatures governed by diffusion-limited crystallite growth. The extent of realized crystallization appears to also be augmented by the use of nanoparticles which may be influential on resultant mechanical properties. The viscosities of the nano-modified blends are nearly an order of magnitude lower than that of the homopolymer as measured in the molten state, indicating a possible disruption of inter-chain contacts and overall degree of hydrogen bonding induced by an increase in free volume concomitant with the dispersion of the nanoparticles.

Experimental observations suggest that the observed acceleration in crystallization kinetics of PEKK due to nanoparticle dispersion is caused by an increase in chain mobility above the glass transition temperature of the polymer in such a way that the particles mobilize free chains to the crystallization growth front. By this mechanism, a high concentration of nanoparticles could be dispelled to the amorphous phase during crystallite growth providing potential added benefits in terms of reinforcement.

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